2006 ERSD Annual Report
DOE-BER Environmental Remediation Sciences Project #1022402

Biogeochemical Coupling of Fe and Tc Speciation in Subsurface Sediments: Implications to Long-Term Tc Immobilization

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Research Objectives:

The project has been focused on biochemical processes in subsurface sediments involving Fe that control the valence state, solubility, and effective mobility of ^{99}Tc. Our goal has been to understand the Tc biogeochemistry as it may occur in suboxic and biostimulated subsurface environments. Two objectives have been pursued:

- To determine the relative reaction rates of $^{99}Tc(VII)O_{2(aq)}$ with metal reducing bacteria and biogenic Fe(II); and to characterize the identity, structure, and molecular speciation of Tc(IV) products formed through reaction with both biotic and abiotic reductants.

- To quantify the biogeochemical factors controlling the reaction rate of O_2 with $Tc(IV)O_2{\cdot}nH_2O$ in sediment resulting from the direct enzymatic reduction of Tc(VII) by DIRB and/or the reaction of Tc(VII) with the various types of biogenic Fe(II) produced by DIRB.

Research Progress and Implications:

Our project team has been supported by ERSD's past NABIR program for five years to investigate the biogeochemical coupling of Fe and Tc speciation in subsurface sediments influenced by the stimulated activity of metal reducing bacteria. Key findings are that: i.) sorbed Fe(II) (of either biotic or abiotic origin) to certain mineral surfaces is extremely reactive with Tc(VII); ii.) sufficient sorbed Fe(II) can exist at circumneutral pH to reduce most environmentally relevant Tc(VII) concentrations even when aqueous Fe(II) is near detection limits; iii.) the heterogeneous reduction process is complex and involves coupling between aqueous and sorbed Fe(II) pools; and iv.) the molecular speciation of Tc(IV) formed by heterogeneous reduction [a Fe(II/III)-Tc(IV) coprecipitate] renders it resistant to oxidation through physicochemical protection. These important findings lead us to conclude that Tc(VII) reduction will occur naturally in reducing microsites in Hanford aquifer sediments created by both abiotic redox reactions with ferrous-containing mineral solids and oxygen-consuming/metal-reducing bacteria.

We have used an oxygen trap to investigate the redox reactivity of sorbed Fe(II) under strictly anoxic conditions on specimen and natural metal oxide and layer silicate surfaces. The experimental design involved (Figure 1): i.) the establishment of a stable $Fe(II)_{aq}$ solution at the desired pH (e.g., pH 7) and concentrations (e.g., 0.12 mM or 0.23 mM) for four days (days -6 to -2); ii.) the addition of a completely deoxygenated solid (e.g., goethite and hematite at day -2)

with monitoring of dissolved and total Fe(II) (by 0.5 N HCl extraction) for two days (-2 to 0), iii.) spiking with a completely deoxygenated Tc(VII) solution (20 μM at 0 day) with subsequent monitoring of $Tc(VII)_{aq}$ for 8 or more days; and iv.) isolation and characterization of the solid-phase redox reaction product by scanning electron microscopy, transmission electron microscopy with electron energy loss spectroscopy (EELS) and selected area electron diffraction (SAED), X-ray absorption spectroscopy [XANES and EXAFS (Figure 2)] and synchrotron diffraction, and Mössbauer spectroscopy.

This specific experiment performed at neutral pH showed rapid and complete reaction of Tc(VII) with sorbed Fe(II) that was not affected by the total Fe(II) concentration or solid structure (Figure 1c). All of the Tc(VII) was converted to surface-associated Tc(IV). Moreover, the heterogeneous redox reaction was accompanied by additional $Fe(II)_{aq}$ sorption (Figure 1b) that rejuvenated the redox reactivity of the surface and created a mixed valence Fe(II)/Fe(III)-Tc(IV) surface coprecipitate. Combinations of Fe isotopes (^{57}Fe; ^{56}Fe) and oxides made from them, isostructural Al oxides (diaspore as a model of goethite and corundum as a model of hematite), and Mössbauer and EXAFS spectroscopy have been used to show that the surface precipitate is a Tc(IV)-containing, Fe(II)-enriched ferrihydrite. Tc-EXAFS measurements of the heterogeneous surface precipitates were identical for hematite and goethite, and these showed that Tc(IV) was imbedded in the Fe(II)-ferrihydrite as a mixture of octahedral monomers (~86%) and dimers (~14%) (Figure 2; Peretyazhko et al., 2006). This speciation scheme differed from that found for Tc(IV) in the redox products of: i.) homogeneous reduction by $Fe(II)_{aq}$ (100% dimers; Zachara et al., 2006a), and ii.) biologic reduction by metal reducing bacteria (extended octahedral chains; Zachara et al., 2006b).

This same approach was used to investigate the heterogeneous reactions of Tc, including both Tc(VII) reduction and Tc(IV) oxidation, on a variety of Fe and Al oxides, and Fe-containing phyllosilicates. The influence of factors such as pH, Fe(II) concentration, and surface complexation strength; as well as structural versus surface Fe(II) association were evaluated. Generally, the heterogeneous reduction of Tc(VII) was found to be fastest on Fe(III) oxides, followed by Al oxides. Heterogeneous reduction rates on phyllosilicates were variable and depend on structural sites of Fe(II) substitution. Reduction rates on all solids decrease with decreasing pH. Ion exchangeable Fe(II) on layer silicates was the least effective reductant for Tc(VII). The heterogeneous oxidation rates of Tc(IV) on all mineral surfaces studied was much slower then for $Tc(IV)O_2 \cdot nH_2O_{(s)}$.

Experiments also investigated the competition between enzymatic and heterogeneous Tc(VII) reduction in anoxic suspensions of metal-reducing bacteria (*Shewanella oneidensis*) and Fe(III) oxides of different types, stabilities, and surface areas (Zachara et al., 2006b). Different electron donors were used to selectively promote either enzymatic Tc(VII) reduction (H_2) or Fe(III) reduction (lactate). In all cases, heterogeneous reduction promoted by small amounts of biogenic Fe(II) outcompeted the enzymatic process, yielding a redox product where Tc(IV) was immobilized in a complex, mixed valence surface precipitate on Fe(III) oxide of different biogenic forms. These experiments lead us to conclude, as a working hypothesis, that heterogeneous Tc(VII) reduction and oxidation will predominate in subsurface biogeochemical systems containing reactive Fe(II).

Planned Activities:

The current project was completed 9/29/06, and a series of final papers is being completed. A new proposal focused on 99Tc was submitted to the 2006 06-12 ERSD call.

Information Access:

Publications

Fredrickson, J. K., J. M. Zachara, D. W. Kennedy, J. P. McKinley, R. K. Kukkadapu, C. Liu, and A. E. Plymale. 2004. Reduction of TcO_4^- by sediment-associated biogenic Fe(II). *Geochim. Cosmochim. Acta* 68(15):3171-3187.

Fredrickson, J. K., J. M. Zachara, S. M. Heald, R. K. Kukkadapu, and D. Moore. 2006. Oxidation rates of Tc(IV) precipitated by heterogeneous reaction with biogenic Fe(II) in subsurface sediments of different mineralogic character. *Geochimica et Cosmochimica Acta* (Submitted).

Kukkadapu, R. K., J. M. Zachara, J. K. Fredrickson, J. P. McKinley, D. W. Kennedy, S. C. Smith, and H. Dong. 2006. Reductive biotransformation of Fe in shale-limestone saprolite containing Fe(III) oxides and Fe(II)/Fe(III) phyllosilicates. *Geochim. Cosmochim. Acta* 70:3662-3676.

Peretyazhko, T, J. M. Zachara, B. -H. Jeon, S. M. Heald, and R. K. Kukkadapu. 2006. Heterogeneous reduction of pertechnetate [Tc(VII)] by sorbed Fe(II) on iron oxides and layer silicate mixtures. *Geochimica et Cosmochimica Acta* (Submitted).

Peretyazhko, T, J. M. Zachara, B. -H. Jeon, S. M. Heald, and R. K. Kukkadapu. 2006. Heterogeneous reduction of pertechnetate [Tc(VII)] by sorbed Fe(II) on aluminum oxide produces a Fe(II/III)-Tc(IV) surface co-precipitate. *Geochimica et Cosmochimica Acta* (In preparation).

Zachara, J. M., S. M. Heald, B. H. Jeon, R. K. Kukkadapu, A. C. Dohnalkova, J. P. McKinley, D. A. Moore, and C. Liu. 2006. Reduction of pertechnetate [Tc(VII)] by aqueous Fe(II) and the nature of solid phase redox products. *Geochimica et Cosmochimica Acta* (Accepted).

Zachara, J. M., J. K. Fredrickson, S. M. Heald, R. K. Kukkadapu, A. C. Dohnalkova, A. Plymale, and D. W. Kennedy. 2006. The relative importance of enzymatic versus heterogeneous reduction of Tc(VII) in suspensions of ferrihydrite and *Shewanella oneidensis*, MR-1. *Environmental Science & Technology* (In preparation).

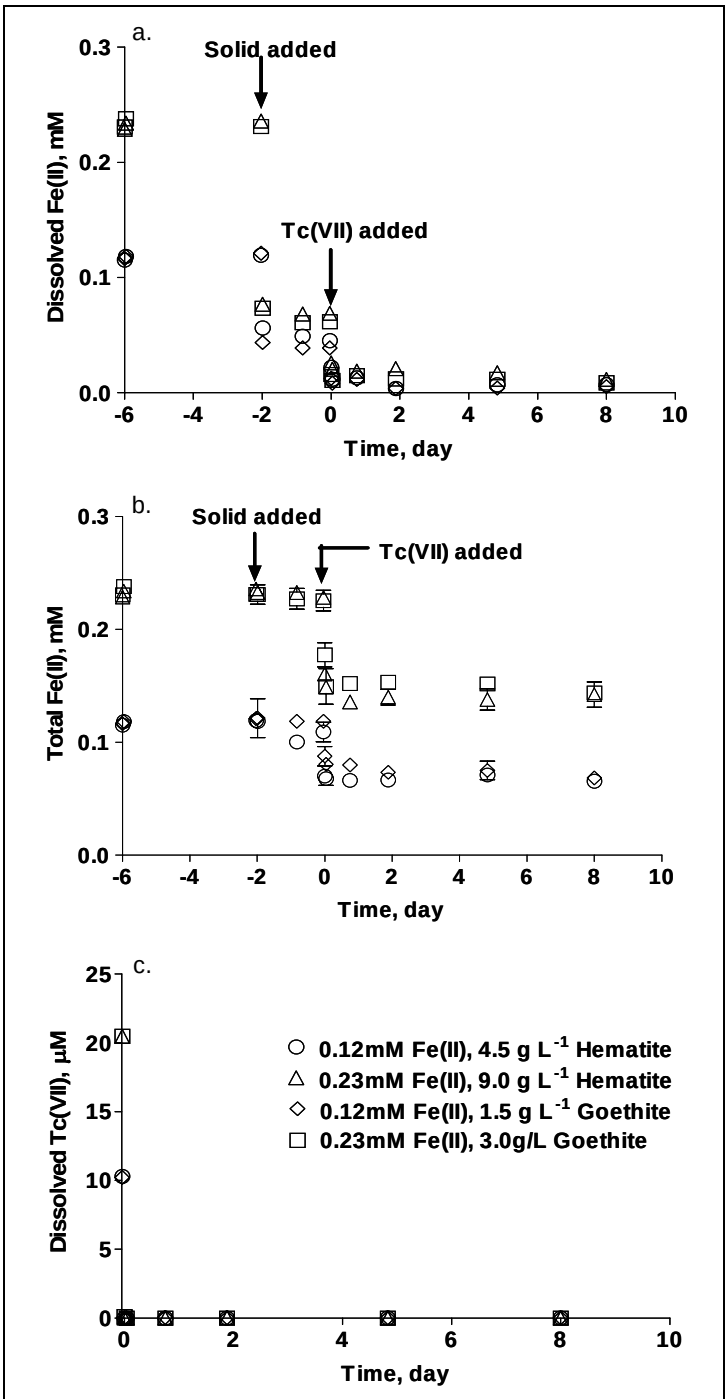

Figure 1. Batch heterogeneous reduction experiment with Tc(VII) and Fe(II)-sorbed goethite and hematite: a.) total Fe(II), b.) aqueous Fe(II), and c.) Tc(VII). Note, the experiment was begun at -6 days, spiked with solid at -2 day, and spiked with Tc(VII) at 0 day.

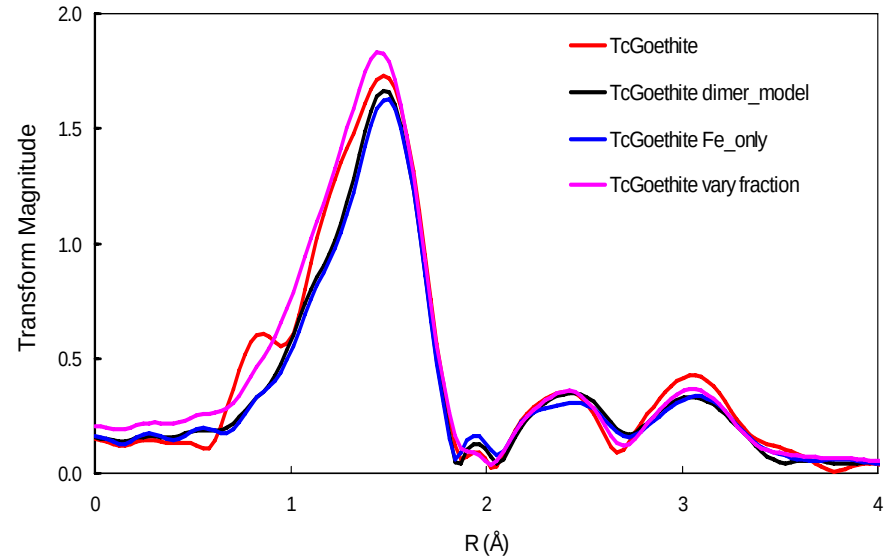

Figure 2. Tc-EXAFS (radial transform) of heterogeneously reduced/ precipitated Tc(IV) on goethite from the experiment in Figure 1. Shown are the data (Tc goethite), and model simulations for Tc(IV) coprecipitated as an octahedral monomer (Fe_only), as an octahedral dimer (dimer_model), and mixture of monomers and dimers (vary fraction). While overall spectral predictions by the three models are quite close, the mixture model yields far superior Debeye-Waller factors that are an indication of improved model correctness.